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<p>(54) Title: OIL ADDITIVES AND COMPOSITIONS</p> <p>(57) Abstract</p> <p>Petroleum fuel antifoams are used to control foaming in blends of petroleum-based fuel oil with biofuel.</p> <p style="text-align: center;">BEST AVAILABLE COPY</p>		

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"Oil Additives and Compositions"

This invention relates to oil compositions, primarily to fuel oil compositions, and more especially to the control of foaming in such compositions.

5 In the processing and transport of hydrocarbon oils, foaming frequently occurs as the oil is passed from one vessel to another. The foaming may interfere with the pumping of the oil, and may be such as to require a reduction in pumping rate to allow foam collapse to avoid oil spills. It is desirable to control foaming to permit higher rates
10 of oil transfer.

The problem of foaming is particularly important in the distribution of oils such as liquid petroleum oils, especially fuel and lubricant oils. Such oils typically pass through a distribution network, involving pumping through pipelines, or a series of storage tanks.

15 Fuel oils derived from vegetable or animal material, also known as biofuels, are believed to be less damaging to the environment on combustion, and are obtained from a renewable resource. Certain biofuels may be used as complete substitutes for fuel oils such as diesel fuel oils. Similarly, certain biofuels may be used as partial substitutes for
20 such fuel oils, being blended into the oils in suitable proportions.

Biofuels per se have lower foaming tendencies than typical fuel oils, such as diesel fuel oils. However, it has unfortunately now been found that blends of a biofuel with a diesel fuel oil have much higher foaming tendencies than the fuel oil per se. This
25 finding is surprising since the minor components of fuel oils believed to be responsible for stabilisation of foam and surface-active in nature, differ from the constituents of these biofuels. Consequently, the addition of a quantity of biofuel to a fuel oil was not expected to increase the foaming tendency of the resulting blend.

30 It has now also surprisingly been found that foaming in a blend of petroleum-based fuel oil and a biofuel may be successfully controlled, in the sense that the initial foam height upon agitation is reduced, by an antifoam additive conventionally used to control foaming in petroleum distillate fuel oils (hereinafter referred to as a petroleum fuel antifoam).

35 Such additives are themselves surface-active in nature, and are believed to interfere in some way with the foam-stabilising tendency of other components of the fuel blend.

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The invention accordingly provides, in a first aspect, a fuel oil composition comprising a major proportion of a blend of petroleum-based fuel oil and a biofuel and a minor proportion of a petroleum fuel antifoam.

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The petroleum fuel antifoams useful in this first aspect of the invention include both silicon-containing, and non silicon-containing, compositions. Where the antifoam is a silicon-containing composition, it has further been found that foaming in the blend of the first aspect may be successfully controlled, in the sense that foam collapse is accelerated, when the blend contains at most 65% by weight of a biofuel.

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The invention accordingly provides, in a preferred embodiment of the first aspect, a fuel oil composition comprising a major proportion of a blend of petroleum-based fuel oil and a biofuel and a minor proportion of a petroleum fuel antifoam being a silicon-containing composition, the fuel oil blend containing at most 65% by weight of a biofuel and at least 35% by weight of a petroleum-based fuel oil.

15

Where the antifoam is a non-silicon containing composition, it has further been found that foaming in the blend of petroleum-based fuel oil and a biofuel may be successfully controlled, in the sense that foam collapse is accelerated, where the blend contains any proportion of biofuel.

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The invention accordingly further provides, in a second preferred embodiment of the first aspect, a fuel oil composition comprising a major proportion of a blend of petroleum-based fuel oil and a biofuel and a minor proportion of a petroleum fuel antifoam being a non silicon-containing composition.

25

In this second preferred embodiment, the antifoam is preferably a product obtainable by the reaction of a polyamine having at least one primary or secondary amino group and a carboxylic acylating agent. The petroleum-based fuel oil advantageously has at least one of the following properties: a specific gravity at 15°C of at most 0.835, preferably at most 0.825; a kinematic viscosity at 20°C of at most 3.10 mm²/s; an IBP of at most 175°C; an FBP of at least 370°C; and a 90%-20% of at least 125°C (the last three characteristics being measured in accordance with ASTM D86).

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Also in this second preferred embodiment, the fuel oil blend advantageously contains at least 60% by weight, and more advantageously more than 65% by weight, of biofuel.

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The invention also provides, in a second aspect, a concentrate comprising a petroleum fuel antifoam in admixture with a blend of a petroleum-based fuel oil and a biofuel; and in a third aspect, the use of a petroleum fuel antifoam to control foaming in a blend of petroleum-based fuel oil and a biofuel.

The invention will hereinafter be described in more detail.

The Petroleum-Based Fuel Oil (of all aspects of the invention)

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The petroleum-based fuel oil is suitably a middle distillate fuel oil, i.e. a fuel oil obtained in refining crude oil as the fraction between the lighter kerosene and jet fuels fraction and the heavier fuel oil fraction. Such distillate fuel oils generally boil within the range of about 100°C to about 500°C (ASTM D-86), e.g. 150°C to about 400°C, for example, those having a relatively high Final Boiling Point of above 360°C, such as 380°C. The fuel oil can comprise atmospheric distillate or vacuum distillate, or cracked gas oil or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates. The most common petroleum distillate fuels are kerosene, jet fuels, diesel fuels, heating oils and heavy fuel oils. The heating oil may be a straight- atmospheric distillate, or it may contain minor amounts, e.g. up to 35 wt%, of vacuum gas oil or cracked gas oils or of both. Heating oils may be made of a blend of virgin distillate, e.g. gas oil, naphtha, etc. and cracked distillates, e.g. catalytic cycle stock. A representative specification for a diesel fuel includes a minimum flash point of 38°C and a 90% distillation point of between 282 and 380°C (see ASTM Designations D-396 and D-975).

25

The fuel oil may have a sulphur concentration of 1% by weight or less based on the weight of the fuel. Preferably, the sulphur concentration is 0.2% by weight or less, more preferably 0.05% by weight or less, and most preferably 0.01% by weight or less. The art describes methods for reducing the sulphur concentration of hydrocarbon middle distillate fuels, such methods including solvent extraction, sulphuric acid treatment, and hydrodesulphurisation.

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The Biofuel (of all aspects of the invention)

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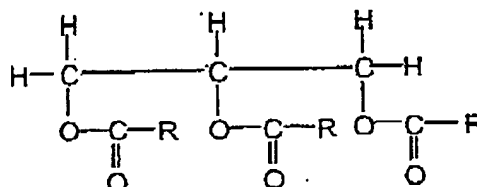
The biofuel may be one or more oils derived from animal or vegetable material or both and capable of being utilised as a fuel.

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Oils obtained from animal or vegetable material are mainly metabolites comprising triglycerides of monocarboxylic acids, e.g. acids containing mainly 10-25 carbon atoms and of the form:



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where R represents an aliphatic radical of predominantly 10-25 carbon atoms which may be saturated or unsaturated. Preferably, R is an aliphatic radical of 10-25 carbons. Generally, such oils contain glycerides of a number of acids, the number and kind
10 varying with the source of the oil, and may additionally contain phosphoglycerides. Such oils may be obtained by methods known in the art.

15

Examples of derivatives of such oils are alkyl esters, such as methyl esters, of fatty acids of the vegetable or animal oils. Such esters can be made by transesterification.

20

Reference within this specification to oils that are derived from animal or vegetable material therefore includes reference both to oils obtained from said animal or vegetable material or both, or to derivatives thereof.

25

Examples of oils derived from animal or vegetable material are rapeseed oil, coriander oil, soyabean oil, cottonseed oil, sunflower oil, castor oil, olive oil, peanut oil, maize oil, almond oil, palm kernel oil, coconut oil, mustard seed oil, beef tallow and fish oils. Further examples include oils derived from corn, jute, sesame, shea nut, ground nut
25 and linseed and may be derived therefrom by methods known in the art. Rapeseed oil, which is a mixture of fatty acids partially esterified with glycerol, is preferred as it is available in large quantities and can be obtained in a simple way by pressing from rapeseed. Rapeseed oil typically contains the esters of, in addition to some 11 to 19% C₁₆ to C₁₈ saturated acids, some 23 to 32% mono-, 40 to 50% di- and 4 to 12% tri-
30 unsaturated C₁₈ to C₂₂ acids, primarily oleic, linoleic, linolenic and erucic acids.

As lower alkyl esters of fatty acids, consideration may be given to the following, for example as commercial mixtures: the ethyl, propyl, butyl and especially methyl esters

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of fatty acids with 12 to 22 carbon atoms, for example of lauric acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, oleic acid, elaidic acid, petroselinic acid, ricinoleic acid, elaeostearic acid, linoleic acid, linolenic acid, eicosanoic acid, gadoleic acid, docosanoic acid or erucic acid, which have an iodine number from 50 to 150, especially 90 to 125. Mixtures with particularly advantageous properties are those which contain mainly, i.e. to at least 50 wt% methyl esters of fatty acids with 16 to 22 carbon atoms and 1, 2 or 3 double bonds. The preferred lower alkyl esters of fatty acids are the methyl esters of oleic acid, linoleic acid, linolenic acid and erucic acid.

Commercial mixtures of the stated kind are obtained for example by cleavage and esterification of animal and vegetable fats and oils by their transesterification with lower aliphatic alcohols. For production of lower alkyl esters of fatty acids it is advantageous to start from fats and oils with high iodine number, such as, for example, sunflower oil, rapeseed oil, coriander oil, castor oil, soyabean oil, cottonseed oil, peanut oil or beef tallow. Lower alkyl esters of fatty acids based on a new variety of rapeseed oil are preferred.

Although many of the above oils may be used as biofuels, preferred are vegetable oils or derivatives thereof, of which particularly preferred biofuels are rapeseed oil, cottonseed oil, soyabean oil, sunflower oil, olive oil, palm oil, or alkyl ester derivatives thereof, rapeseed oil methyl ester being especially preferred.

The Blend (of all aspects of the invention)

The proportion of biofuel in the blend may range from 0.1% to 99.9%, preferably from 0.1% to 90% and more preferably from 0.5% to 85%, by weight. Where the antifoam is a silicon-containing composition, the proportion by biofuel is advantageously at most 65%, and more advantageously at most 55%, by weight. Where the antifoam is a non silicon-containing composition, the proportion of biofuel is advantageously at least 60%, more advantageously more than 65%, by weight.

It is within the scope of the invention to use, as the blend, two or more petroleum-based fuel oils, or more especially two or more biofuels, in admixture with one or more of the other type of fuel.

The blend may contain additives other than the petroleum fuel antifoam. Thus, one or more co-additives such as low temperature flow improvers, stabilisers, dispersants, antioxidants, corrosion inhibitors, cetane improvers, emissions-reducing

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agents, reodorants, lubricity agents, antistatic additives or demulsifiers may be present in the blend. These co-additives may be added to the blend simultaneously with the petroleum fuel antifoam; for example, the antifoam and co-additives may comprise a single additive. Alternatively, one or more co-additives may be added to the blend independent of the antifoam, or to the petroleum-based fuel oil or biofuel prior to blending.

The Petroleum Fuel Antifoam (of all aspects of the invention)

The antifoam is advantageously insoluble in the fuel being treated but is dispersible therein to form a stable dispersion, if necessary with the aid of a suitable dispersant or solvent, either with or without the use of mechanical dispersing aids.

As the antifoam there may, as indicated above, be used a silicon-containing composition. Such a composition advantageously comprises a siloxane polymer, for example a block copolymer containing siloxane blocks and oxyalkylene blocks. Preferred as such siloxane polymers are those of general formula (i)



wherein R represents a hydrocarbyl group, n represents an integer in the range of 1 to 3 and m represents a number ≥ 2 . The hydrocarbyl group may be a relatively simple hydrocarbyl group of from 1 to 30 carbon atoms or may be a polymeric group. The groups represented by R may be the same or different in any given siloxane group or throughout the siloxane polymer and the value of n in the various siloxane groups in the siloxane polymer may be the same or different.

The preferred polymers are block co-polymers comprising at least two blocks, one block comprising siloxane groups as represented by general formula (i) and the second block comprising oxyalkylene groups of general formula (ii)



The siloxane block and the oxyalkylene block may be linked to each other by means of a divalent hydrocarbyl group; this may be R in general formula (i). Hence each siloxane block contains at least one group represented by general formula (i) wherein at

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least one group represented by R is a divalent hydrocarbyl group. The siloxane block has a ratio of hydrocarbyl groups to silicon atoms of 1:1 to 3:1.

The hydrocarbyl groups that are represented by R in general formula (i) may be alkenyl groups for example vinyl and allyl; cycloalkenyl groups, for example cyclohexenyl; alkyl groups, for example methyl, ethyl, isopropyl, octyl and dodecyl; aryl groups, for example phenyl and naphthyl; aralkyl groups, for example benzyl and phenylethyl; alkaryl groups, for example styryl, tolyl and n-hexylphenyl; or cycloalkyl groups, for example cyclohexyl.

The divalent hydrocarbyl groups represented by R in general formula (i) may be alkylene groups such as methylene, ethylene, propylene, butylene, 2,2-di-methyl-1,3-propylene and decylene, arylene groups such as phenylene and p,p'-diphenylene, or alkarylene groups such as phenylethylene. Preferably the divalent hydrocarbyl group is an alkylene group containing from two to four successive carbon atoms.

These divalent hydrocarbyl groups are linked to a silicon atom of the siloxane block by a silicon-to-carbon bond and to an oxygen atom of the oxyalkylene block by a carbon-to-oxygen bond.

The siloxane block in the copolymers may contain siloxane groups that are represented by general formula (i) wherein either the same hydrocarbyl groups are attached to the silicon atoms (e.g. the dimethylsiloxo, diphenylsiloxo and diethylsiloxo groups) or different hydrocarbyl groups are attached to the silicon atoms (e.g. the methylphenylsiloxo, phenylethylmethylsiloxo and ethylvinylsiloxo groups).

The siloxane block in the copolymers may contain one or more types of siloxane group that are represented by general formula (i) provided that at least one group has at least one divalent hydrocarbyl substituent. By way of illustration only, ethylenemethylsiloxo groups can be present in the siloxane block or the siloxane block can contain more than one type of siloxane group, e.g. the block can contain both ethylenemethylsiloxo groups and diphenylsiloxo groups, or the block can contain ethylenemethylsiloxo groups, diphenylsiloxo groups and diethylsiloxo groups.

The siloxane block may contain trifunctional siloxane groups (e.g. monomethylsiloxane groups, $\text{CH}_3\text{SiO}_{1.5}$), difunctional siloxane groups (e.g. dimethylsiloxane groups, $(\text{CH}_3)_2\text{SiO}$), monofunctional siloxane groups (e.g. trimethylsiloxane groups, $(\text{CH}_3)_3\text{SiO}_{0.5}$) or combinations of these types of siloxane

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groups having the same or different substituents. Due to the functionality of the siloxane groups, the siloxane block may be predominantly linear or cyclic or crosslinked, or it may have combinations of these structures.

5 The siloxane block may contain organic end-blocking or chain-terminating organic groups in addition to the monofunctional siloxane chain-terminating groups encompassed by general formula (i). Organic end-blocking groups may be hydroxyl groups, aryloxy groups such as phenoxy, alkoxy groups such as methoxy, ethoxy, propoxy and butoxy, and acyloxy groups such as acetoxo.

10 The siloxane blocks in the copolymers contain at least two siloxane groups that are represented by general formula (i) (so that m represents a number ≥ 2). Preferably, the siloxane blocks contain a total of from five to twenty siloxane groups that are represented by general formula (i), with m representing a number in the range of 5 to 20.
15 That part of the average molecular weight of the copolymer that is attributable to the siloxane blocks may be as high as 50000 but preferably it is from 220 to 20000. If that part of the average molecular weight of the copolymer that is attributable to the siloxane blocks exceeds 50000 or if the siloxane blocks contain a total of more than twenty siloxane groups that are represented by general formula (i), the copolymers are usually
20 not as useful, e.g. they may be too viscous for convenient use in the additives of this invention.

 The oxyalkylene blocks in the copolymers each contain at least two oxyalkylene groups that are represented by the general formula (ii) wherein R^1 is an alkylene group.
25 Preferably, at least 60 per cent by weight of such groups represented by general formula (ii) are oxyethylene or oxypropylene groups.

 Other oxyalkylene groups that are represented by general formula (ii) which can also be present in the oxyalkylene block, preferably in amounts not exceeding 40 per
30 cent by weight are oxy-1,4-butylene, oxy-1,5-amylene, oxy-2,2-dimethyl-1,3-propylene, or oxy-1,10-decylene groups.

 The oxyalkylene blocks in the copolymers may contain oxyethylene or oxypropylene groups alone or along with one or more of the various types of oxyalkylene
35 groups represented by general formula (ii); the oxyalkylene blocks can contain only oxyethylene groups or only oxypropylene groups or both oxyethylene and oxypropylene groups, or other combinations of the various types of oxyalkylene groups represented by general formula (ii).

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The oxyalkylene blocks in the copolymers may contain organic end-blocking or chain-terminating groups. Such end-blocking groups may be hydroxy groups, aryloxy groups such as phenoxy, alkoxy groups such as methoxy, ethoxy, propoxy and butoxy, and alkenyloxy groups such as vinyloxy and allyloxy. A single group can serve as an end-blocking group for more than one oxyalkylene block; for example, the glyceroxy group can serve as an end-blocking group for three oxyalkylene chains.

The oxyalkylene blocks in the copolymers contain at least two oxyalkylene groups that are represented by general formula (ii). Preferably, each block contains from four to thirty of such groups. That part of the average molecular weight of the copolymer that is attributable to the oxyalkylene blocks can vary from 176 (for $(C_2H_4O)_4$) to 200000, but preferably it is from 176 to 15000. Provided that each oxyalkylene block contains at least two oxyalkylene groups represented by general formula (ii), the number of oxyalkylene groups and that part of the average molecular weight of the copolymer that is attributable to the oxyalkylene blocks is not critical, providing that the resulting copolymer is not rendered physically incompatible with oleaginous liquids. However, those copolymers in which that part of the average molecular weight that is attributable to the oxyalkylene blocks exceeds 200000 or that contain more than fifty oxyalkylene groups per block prove less useful, e.g. they are too viscous for convenient use in the additives of this invention.

The copolymers may contain siloxane blocks and oxyalkylene blocks in any relative amounts. In order to possess desirable properties, the copolymer should contain from 5 parts by weight to 95 parts by weight of siloxane blocks and from 5 parts by weight to 95 parts by weight of oxyalkylene blocks per 100 parts by weight of the copolymer. Preferably, the copolymers contain 5 parts by weight to 50 parts by weight of the siloxane blocks and from 50 parts by weight to 95 parts by weight of the oxyalkylene blocks per 100 parts by weight of the copolymer.

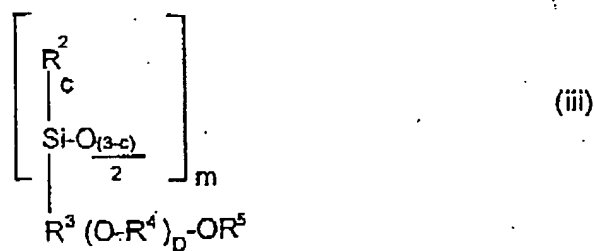
The copolymers may contain more than one of each of the blocks and the blocks may be arranged in various configurations such as linear, cyclic or branched configurations.

The most preferred block co-polymers have the general formula (iii)

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wherein p represents an integer ≥ 2 and preferably represents an integer in the range of 4 to 30, c represents an integer in the range of 0 to 2, m represents an integer ≥ 2 , R^2 represents a monovalent hydrocarbyl radical of 1 to 12 carbon atoms preferably a linear aliphatic radical for example a methyl or ethyl group, R^3 represents a divalent hydrocarbyl radical of 1 to 12 carbon atoms preferably an alkylene group of at least two carbon atoms for example ethylene, 1,3-propylene or 1,4-butyene, R^4 represents the same or different divalent hydrocarbyl radicals of 2 to 10 carbon atoms such as for example ethylene, 1,3-propylene or 1,6-hexylene, and R^5 represents a monovalent hydrocarbyl group of 1 to 12 carbon atoms or an end-group such as for example hydroxyl or hydrogen. It is preferred that R^4 represents different hydrocarbyl radicals and most preferably represents a mixture of at least one of each of ethylene and 1,3-propylene radicals.

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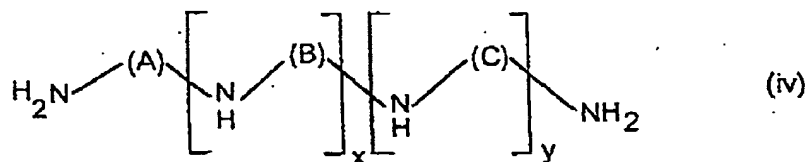
The above-described block copolymers may be produced by an addition reaction between siloxanes containing silicon-bonded hydrogen atoms and oxyalkylene polymers containing alkenyl end-blocking groups in the presence of a platinum catalyst. These copolymers can also be prepared by a metathesis reaction between siloxanes containing silicon-bonded chloro-organo groups and an alkaline metal salt of a hydroxy end-blocked oxyalkylene polymer.

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As the antifoam there may, alternatively, be used a non-silicon containing composition comprising a product obtainable by the reaction between:

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(a) a polyamine of the formula (iv)



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wherein A, B, C are the same or different and each represents a hydrocarbylene group, and x and y are integers whose sum is in the range of 0 to 10, and

(b) a carboxylic acylating agent.

5

Advantageously, the sum of x and y is in the range from 1 to 10. More advantageously, the sum of x and y is not more than 8, preferably not more than 6, more preferably not more than 4 and most preferably not more than 2.

10

As used in this specification the term "hydrocarbyl" refers to a group having a carbon atom directly attached to the rest of the molecule and having a hydrocarbon or predominantly hydrocarbon character. Among these, there may be mentioned hydrocarbon groups, including aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, aliphatic and alicyclic-substituted aromatic, and aromatic-substituted aliphatic and alicyclic groups. Aliphatic groups are advantageously, 15 saturated. Unsubstituted hydrocarbyl groups are preferred; however, if desired such groups may carry further hydrocarbyl groups as substituents. Such groups may also contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group, examples include keto, halo, 20 hydroxy, nitro, cyano, alkoxy and hydroxyalkyl. If the hydrocarbyl group is substituted, a single (mono) substituent is preferred. Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for 25 example, nitrogen, sulfur, and, preferably oxygen. Advantageously, each hydrocarbyl group contains at most 10, preferably at most 8, more preferably at most 6 and most preferably at most 4, carbon atoms.

The term "hydrocarbylene" is used analogously.

30

In a preferred embodiment of the non-silicon antifoam, the polyamine reactant is an alkylene diamine, or polyalkylene polyamine of the above formula where A, B and C are each alkylene groups containing up to 10, preferably at most 8, more preferably at most 6 and most preferably at most 4, carbon atoms. Thus the polyamine reactants 35 preferred in the present invention include simple diamines, for example ethylene diamine, propylene diamine, butylene diamine and pentylene diamine; polyalkylene polyamines for example diethylene triamine, triethylene diamine, tetraethylene

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pentamine, pentaethylene hexamine, di(methylethylene)triamine, dibutylene triamine, tributylene tetramine and dipentylene hexamine.

5 The alkylene groups constituting A, B and C may optionally be substituted by one or more hydrocarbyl groups as hereinbefore described. In a more highly preferred embodiment, A, B and C are alkylene groups containing 1 to 3 carbon atoms, optionally substituted by one or more alkyl, alkenyl, alkoxy or hydroxyalkyl groups with hydroxyalkyl groups being most preferred. Most highly preferred embodiments of the polyamines suitable as reactant (a) include ethylene diamine and diethylene triamine.

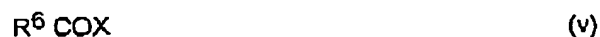
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The polyamine reactant may comprise a mixture of polyamines, each component being a polyamine having the aforesaid general formula (iv). Of such mixtures, those comprising alkylene diamines and polyalkylene polyamines are preferred, such amines being optionally substituted by one or more hydrocarbyl groups. More preferred are mixtures comprising alkylene diamines and polyalkylene polyamines wherein said 15 alkylene groups contain 1-3 carbon atoms, optionally substituted by one or more alkyl, alkenyl, alkoxy or hydroxyalkyl groups. Most highly-preferred mixtures of polyamines include mixtures of ethylene diamine, diethylene triamine.

20

The carboxylic acylating agents useful as reactant (b) contain one or more carboxylic acylating groups, and a hydrocarbyl group sufficient to impart hydrocarbon solubility to the molecule. Suitable carboxylic acylating groups include carboxylic acid groups and derivatives thereof possessing a leaving group, i.e. a group capable of being displaced during reaction. Examples of such carboxylic derivatives include esters, 25 anhydrides and acyl halides including acyl chlorides, acyl bromides and acyl iodides, although other carboxylic derivatives known in the art as acylating agents may be used to equal effect.

30 More preferred carboxylic acylating agents are monocarboxylic acylating agents of the formula (v):



35 where R^6 represents a hydrocarbyl group, and where X represents a leaving group. Such preferred agents include fatty acid compositions, such as naturally-occurring fatty acids and derivatives of same. Preferably, such fatty acids or derivatives contain from 8 to 40, more preferably 10 to 30, even more preferably 12 to 24, and most preferably 12 to 18 carbon atoms. In such fatty acid compositions, R^6 is preferably

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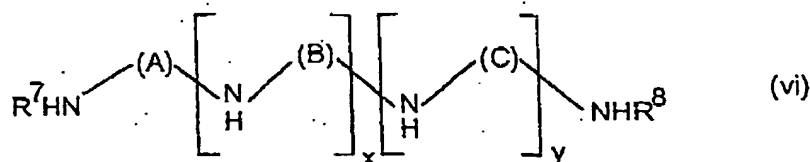
straight or branched-chain alkyl or alkenyl. Most preferred fatty acids include those selected from the group comprising lauric, myristic, palmitic, stearic, oleic, cecanoic and coco-fatty acids, the last four acids or mixtures thereof being most preferred.

5 The preferred fatty acid compositions may also comprise mixtures of fatty acids, having an average carbon number within the preferred ranges hereinbefore described. Such specifically-preferred mixtures include mixtures of the above fatty acids, and naturally-originating mixtures such as coco-fatty acid fraction and cecanoic acid (a mixture of iso-C₁₃ fatty acids). Mixtures of naturally-originating fatty acids with the other
10 fatty acids described above are also preferred.

The products of reaction may be of mixed composition. Thus, the product may comprise a mixture of simple amides, di- and higher poly-amides, imides and/or amidine reaction products where the nature of reactants (a) and (b) and the ratio in which they
15 are combined permits such reactions to take place. Their definition in terms of reaction products thus describes most conveniently the range of possible compositions obtained in accordance with this invention.

Reaction conditions suitable for generating the above reaction products are for
20 example known in the art for promoting the acylation of polyamines. Thus, the reaction may be carried out by mixing the reactants (a) and (b), optionally combined in the presence of a mutual co-solvent, and heating the mixture sufficiently to cause reaction to occur, without raising the temperature above the decomposition temperature of the reactants or product. Alternatively, reactant (a) may be heated to reaction temperature
25 and reactant (b) added over an extended period. Suitable temperatures are typically between 100°C and 300°C, the exact temperature being determined by the nature of the selected reactants. Examples of the preparation of products according to this invention are found in US 4,394,135, and EP 147,240, to which further attention is directed.

30 A further class of non-silicon antifoams in accordance with this invention are those obtainable by the reaction of the carboxylic acylating agent (b) as hereinbefore described with one or more polyamines (a) of the general formula (vi)



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wherein A, B and C are as hereinbefore defined and herein R^7 and R^8 maybe the same or different and each represents hydrogen or a hydrocarbyl group, provided that both R^7 and R^8 are not hydrogen, and x and y are integers whose sum is in the range from 0 to 10.

In a preferred embodiment, the polyamine reactant is a terminal N-substituted or terminal N,N'-disubstituted polyamine of the formula (vi) wherein A, B and C are each alkylene groups containing up to 10, preferably at most 8, more preferably at most 6 and most preferably at most 4, carbon atoms. Thus these polyamine reactants include terminal N-substituted or terminal N,N'-disubstituted derivatives of simple diamines such as ethylene diamine, propylene diamine, butylene diamine and pentylene diamine, and terminal N-substituted, or terminal N,N'-disubstituted derivatives of polyalkylene polyamines such as diethylene triamine, triethylene diamine, tetraethylene pentamine, pentaethylene hexamine, di(methylethylene)triamine, dibutylene triamine, tributylene tetramine and dipentylene hexamine.

In a more preferred embodiment, R^7 and R^8 of the polyamine reactant each independently represent hydrogen or an aliphatic hydrocarbyl group. This aliphatic hydrocarbyl group is preferably a straight or branched chain alkyl, oxyalkyl or hydroxyalkyl group. Most preferably, it is a hydroxyalkyl group, for example a 2-hydroxyethyl group.

Particularly preferred amines are those in which one of R^7 and R^8 is hydrogen. Also advantageously, the sum of x and y in the polyamine is not more than 8, preferably not more than 6, more preferably not more than 4 and most preferably not more than 2.

The polyamine reactant may comprise a mixture of polyamines, each component being a polyamine having the aforesaid general formula. Of such mixtures, those comprising terminal N-substituted or terminal N,N'-disubstituted alkylene diamines, and terminal N-substituted or terminal N,N'-disubstituted polyalkylene polyamines are preferred, such amines being optionally substituted by one or more hydrocarbyl groups. Most preferred are mixtures comprising alkylene diamines and polyalkylene polyamines wherein said alkylene groups contain 1-3 carbon atoms, optionally substituted by one or more alkyl, alkenyl, alkoxy or hydroxyalkyl groups.

The polyamine reactant may also comprise a mixture of polyamines of the formula (iv) in combination with a mixture of polyamines of the formula (vi).

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The degree of acylation of polyamine (a) is generally dictated by the number of primary and secondary nitrogens present within the polyamine, i.e. the number of possible acylation sites, the proportions in which reactants (a) and (b) are mixed, and the time allowed for reaction. The product may be formed by the reaction of one mole of polyamine with at least one mole of the carboxylic acylating agent. Preferably, the product is formed by the reaction of one mole of polyamine with at least two moles of the carboxylic acylating agent. More preferably, the product is formed by the full acylation of the polyamine by the carboxylic acylating agent. Within this specification, the term 'full' acylation is used to define reactions where every amino group on the polyamine has undergone a condensation reaction upon addition of acylating agent (b). Thus, under 'full' acylation, each polyamine amino group will react to evolve one equivalent of water, irrespective of the exact nature of the condensation reaction which occurs with the acylating agent (b).

Particularly preferred embodiments of the non silicon-containing antifoam are those in which the product may be obtained by the reaction between one mole of the polyamine of the formula (iv) or (vi) as hereinbefore defined with at least two moles of the monocarboxylic acylating agent of the formula (v) also hereinbefore defined. Most advantageous are those products which may be obtained by the full acylation of said polyamine by said acylating agent.

In accordance with all aspects of the invention, the concentration of the antifoam in the fuel oil composition may for example be in the range of 0.1 to 10,000 ppm, preferably 0.5 to 5000 ppm and most preferably 1 to 100 ppm (active ingredient) by weight per weight of fuel oil. Particularly advantageous concentrations are in the range of 1 to 20 ppm.

Concentrate

Concentrates are convenient as a means for incorporating the antifoam into the bulk fuel blend. Incorporation may be by methods known in the art. The concentrates may also contain co-additives as required and as hereinbefore described and preferably contain from 3 to 75 wt%, more preferably 3 to 60 wt%, most preferably 10 to 50 wt% of the additives preferably in solution in oil. Examples of carrier liquids are organic solvents including hydrocarbon solvents, for example petroleum fractions such as naphtha, kerosene, diesel and heater oil; aromatic hydrocarbons such as aromatic fractions, e.g. those sold under the 'SOLVESSO' trade name; and paraffinic hydrocarbons such as

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hexane and pentane and isoparaffins. The carrier liquid must, of course, be selected having regard to its compatibility with the additives and with the fuel blend.

In accordance with the second aspect of the invention, suitable as such a carrier liquid is the fuel blend into the bulk of which the concentrate will be incorporated.

The antifoam may be incorporated into the bulk fuel blend by other methods such as those known in the art. Co-additives may be incorporated into the bulk fuel blend at the same time as the antifoam or at a different time.

The invention will now be illustrated by way of example only as follows:

Fuels used in the examples

Two petroleum-based fuel oils and a biofuel, having the characteristics shown in Table 1, were used in the following examples of the invention. Both fuel oils were diesel fuels whilst the biofuel was rapeseed methyl ester.

Table 1

Fuel Characteristics	Fuel Oil A	Fuel Oil B	Biofuel
Density, g/ml, 15°C	0.82	0.85	0.88
Viscosity, 20°C, mm ² /s	3.09	4.7	7.22
ASTM-D86 Distillation: (°C)			
IBP	168	188	
20%	203	230	
90%	330	329	
FBP	371	362	
90-20	127	90	
90-FBP	41	33	
Cloud Point, °C (I.S.O. 3015)	-3	-5	-4
CFPP, °C (E.N. 116)	-5	-4	-14

Examples of Antifoams useful in the invention

(i) Non silicon-containing compositions:-

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Example 1

Oleic acid (282 g; 1.0 moles) was dissolved in toluene (250 mls). Diethylene triamine (DETA) (34.3 g; 0.33 moles) was dissolved in toluene (100 mls), the slight stoichiometric excess of DETA being used to ensure subsequent acylation of every amino-group. The amine solution was added slowly to the stirred solution of the acid over one hour. During this addition there was an exotherm and the reaction temperature increased by 13°C. When the addition of the amine was complete, the reaction mixture was heated to reflux for 7 hours and 45 minutes. During the reflux water (17 mls; theory = 18 mls) was collected in a Dean & Stark trap. At the end of the reflux the toluene was removed by distilling the reaction mixture to a pot temperature of 150°C. Final traces of solvent were removed from the product by applying a vacuum of 500 mm Hg.

The product obtained was a waxy solid. The IR spectrum of the product showed no trace of oleic acid (peak at 1711 wavenumbers). There were, however, peaks at 1665 and 1590 wavenumbers consistent with the formation of secondary and tertiary amine groups, i.e. that acylation had been essentially full.

Examples 2 and 3

Analogous reaction conditions were employed to generate the fully-acylated reaction products as illustrated in Table 2 below.

Table 2

Ex. No.	Reactants		Ratio of a:b used
	(a) polyamine	(b) monocarboxylic acylating agent	
2		oleic acid	slightly greater than 1:4
3		tall-oil fatty acid	slightly greater than 1:3

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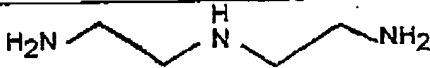
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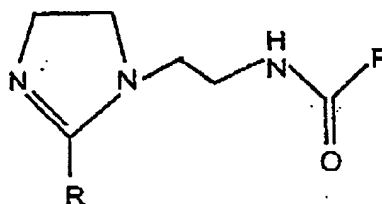
Examples 4 and 5

Reaction conditions analogous to those used for the synthesis of the previous examples 1-3 were employed in the reaction of one mole of diethylene triamine with two moles of monocarboxylic acylating agent, as shown in Table 3.

Table 3

Example No.	Reactants	
	(a) polyamine	(b) monocarboxylic acylating agent
4		stearic acid
5		tall-oil fatty acid

In both examples, the major product was of the form



where the acylating agent (b) corresponds to RCOOH, i.e. still a fully-acylated product within the meaning of this specification, every amino group of the polyamine having undergone reaction upon addition of acylating agent (b) and three moles of water per mole of DETA having been evolved.

Examples 6 to 14


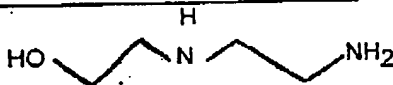
Reaction conditions analogous to those used for the synthesis of Examples 1-3 were employed to generate the products illustrated in Table 4 below.

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Table 4

Example No.	Reactants	
	(a) polyamine	(b) monocarboxylic acylating agent
6		stearic acid
7	- "	oleic acid
8	- "	cecanoic acid
9	- "	coco fatty acid
10	- "	tall-oil fatty acid
11	- "	1:1 mixture of coco and tall-oil fatty acids
12		coco fatty acids
13	- "	cecanoic acid
14	- "	stearic acid

In each example, one mole of polyamine was reacted with slightly in excess of two moles of acylating agent.

(ii) Silicon-containing compositions:-

Antifoam A - a proprietary block copolymer comprising siloxane blocks and oxyalkylene blocks, and of the general class hereinbefore described. Antifoam A is sold commercially for the treatment of middle distillate fuel oils.

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Example of the Invention:

The fuel oil compositions defined in Table 5 were prepared by a conventional laboratory blending technique, using a WARING blender. The foaming tendency of each blend of biofuel and petroleum-based fuel oil was measured following addition of antifoam example 4 or antifoam A, using a test procedure involving the agitation by hand of 100 ml of test fuel oil in a previously-cleaned and dried 4 oz bottle, the bottle then being placed in normal attitude on a stationary, flat surface. The subsequent length of time (in seconds) over which the foam generated by shaking collapsed sufficiently to reveal a clear area of liquid surface was recorded as one measure of foaming tendency, longer foam collapse times indicating greater foam stability.

As indicated by the results in Table 5, the non silicon-containing antifoam significantly reduced foam collapse time in all blends comprising fuel oil A, and in those blends comprising fuel oil B and at least 60% of biofuel (by wt.)

The silicon-containing antifoam significantly reduced foam collapse time in all blends comprising fuel oil A and at most 60% of biofuel (by wt.), and in all blends comprising fuel oil B and at most 70% of biofuel (by wt.) These results suggest the silicon-containing antifoam to be generally effective in fuel oil blends comprising at most about 65% biofuel (by wt.).

The foaming tendency of each blend in Table 5 was also measured in terms of the initial foam height obtained upon agitation. In Table 5, the foam height of each antifoam-containing fuel oil composition is shown (in parentheses) as a percentage of the foam height of the corresponding untreated blend.

The blend foam height results show that initial foam height is generally reduced upon addition of a petroleum fuel antifoam.

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Table 5

Proportion of Biofuel in Blend, (% wt)	Petroleum based Fuel Oil					
	Fuel Oil A: Foam Collapse Time, secs (% foam height)			Fuel Oil B: Foam Collapse Time, secs (% foam height)		
	Untreated	+ Antifoam 4 at 10 ppm, w/w	+ Antifoam A at 12.5 ppm, w/w	Untreated	+ Antifoam 4 at 10 ppm, w/w	+ Antifoam A at 12.5 ppm, w/w
0	17.5	16.0 (50)	0 (15)	39	6 (50)	0 (5)
10	38.5	30 (60)	0 (15)	41.5	45.5 (70)	0 (5)
20	43	25.5 (60)	0 (15)	48.5	59.5 (70)	9.5 (5)
30	39.5	37 (70)	11 (50)	55.5	54.5 (70)	20.5 (10)
40	41	36 (70)	14.5 (40)	59	68.5 (100)	27 (10)
50	54.5	43 (100)	21.5 (50)	64	68 (100)	43.5 (20)
60	52	34.5 (60)	31.5 (50)	68	55.5 (80)	54.5 (40)
70	40	25.5 (60)	55 (70)	66	45 (50)	65 (40)
80	28.5	20 (60)	70 (100)	74	30.5 (50)	91 (60)
90	15	10.5 (50)	77 (100)	73.5	16 (50)	118.5 (60)
100	0	0 (-)	0 (-)	0	0 (-)	0 (-)

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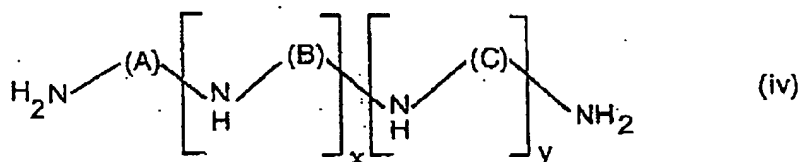
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Claims:

1. A fuel oil composition comprising a major proportion of a blend of petroleum-based fuel oil and a biofuel and a minor proportion of a petroleum fuel antifoam.
2. A composition as claimed in claim 1, wherein the antifoam is silicon-containing composition.
3. A composition as claimed in claim 2, wherein the silicon-containing composition comprises a block copolymer containing siloxane blocks and oxyalkylene blocks.
4. A composition as claimed in claim 2 or claim 3, wherein the fuel oil blend contains at most 85% by weight of a biofuel and at least 35% by weight of a petroleum-based fuel oil.
5. A composition as claimed in claim 1, wherein the antifoam is a non silicon-containing composition.
6. A composition as claimed in claim 5, wherein the antifoam is a product obtainable by the reaction between a polyamine having at least one primary or secondary amino group and a carboxylic acylating agent.
7. A composition as claimed in claim 5 or claim 6, wherein the reaction product is one obtainable by reaction between:

- a) a polyamine of the formula (iv)



- b) and a monocarboxylic acylating agent of the formula (v)



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wherein A, B and C, which may be the same or different, represent hydrocarbylene groups and R^G represents a hydrocarbyl group, X is a leaving group, and x and y are integers whose sum is in the range from 0 to 10.

5

8. A composition as claimed in claim 7, wherein the reaction product is obtainable by the reaction between one mole of the polyamine and at least two moles of the monocarboxylic acylating agent.

10

9. A composition as claimed in claim 7 or claim 8, wherein the reaction product is obtainable by the full acylation of the polyamine by the monocarboxylic acylating agent.

15

10. A composition as claimed in any of claims 7 to 9, wherein the product is obtainable by the reaction between a polyalkylene polyamine and a monocarboxylic acylating agent selected from the group comprising stearic acid, oleic acid, cecanoic acid and a coco-fatty acid fraction, or a mixture thereof.

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11. A composition as claimed in claim 10, wherein the product is obtainable by the reaction between diethylene triamine and stearic acid.

12. A composition as claimed in any one of claims 5 to 11, wherein the fuel oil blend contains at least 60% of biofuel.

25

13. A composition as claimed in claim 12, wherein the fuel oil blend contains more than 65% of biofuel.

30

14. A composition as claimed in any one of claims 1 to 13, wherein the biofuel is a rapeseed methyl ester.

15. A composition as claimed in any one of claims 1 to 14, wherein the petroleum-based fuel oil is a middle distillate petroleum fraction.

35

16. A composition as claimed in any one of claims 1 to 15, which comprises from 0.5 to 5000 ppm by weight of antifoam.

17. A concentrate comprising a petroleum fuel antifoam in admixture with a blend of petroleum-based fuel oil and a biofuel.

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18. The use of a petroleum fuel antifoam to control foaming in a blend of petroleum-based fuel oil and a biofuel.

INTERNATIONAL SEARCH REPORT

Intern. Application No.
PCT/EP 94/00550A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C10L1/22 C10L1/28 C10L1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WD,A,94 06894 (EXXON) 31 March 1994 see page 13, line 9 - line 15	1,5-18
X	US,A,2 862 885 (NELSON ET AL.) 2 December 1958	1,2, 15-18 4
Y	see column 6, line 45 - line 75	
Y	FR,A,2 579 481 (DOW CORNING) 3 October 1986 see the whole document	1-4, 15-18
P,Y	US,A,5 192 336 (GREWAL) 9 March 1993 see the whole document	1,5-10, 12-18
X	GB,A,658 494 (SHELL) 10 October 1951 see page 5, line 32 - line 54	1,5-13, 15-18

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Date of the actual completion of the international search

16 May 1994

Date of mailing of the international search report

26. 05. 94

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INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/EP 94/00550

C/(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,4 364 743 (ERNER) 21 December 1982 see the whole document	1-10, 12-18
A	FR,A,1 584 938 (BASF) 2 January 1970 see the whole document	1,5-18

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.
PCT/EP 94/00550

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US-A-2862885		BE-A- 544303 FR-A- 1146658 GB-A- 814200	
FR-A-2579481	03-10-86	AU-B- 584408 BE-A- 904498 CA-A- 1272599 DE-A- 3610414 GB-A, B 2173510 JP-A- 61225283 NL-A- 8600571 SE-A- 8601211 US-A- 4690688	25-05-89 16-07-86 14-08-90 02-10-86 15-10-86 07-10-86 16-10-86 30-09-86 01-09-87
US-A-5192336	09-03-93	NONE	
GB-A-658494		FR-A- 1018772	
US-A-4364743	21-12-82	NONE	
FR-A-1584938	02-01-70	NONE	

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